Scattering from block copolymer systems is characterized by a scattering peak representing the average inter-distance between domains in the ordered phase region. The scattering peak persists in the disordered phase region where it represents the "correlation hole" effect (Leibler, 1980). Scattering from a diblock copolymer solution is discussed here.

1. POLYSTYRENE-POLYISOPRENE COPOLYMER IN DOP SOLUTION

The polystyrene-polyisoprene (hPS-hPI) diblock copolymer considered here has typical molecular weights (M_w=11,000 for hPS and M_w=17,000 g/mol for hPI). Since the order-to-disorder phase transition temperature (ODT) for this copolymer is high, it was dissolved in dioctyl phthalate (DOP) at a copolymer volume fraction of 0.65. This brought the ODT down to an easily reachable value. DOP is a non-volatile good solvent for both hPS and hPI.

Even though none of the blocks is deuterated, the hPS-hPI copolymer is characterized by a reasonable "natural" neutron contrast in DOP.

Table 1: Summary of the scattering lengths and specific volumes.

	Notation	Formula	Scattering Length (cm)	Density (g/cm^3)	Specific Volume (cm^3/mol)
Polystyrene	hPS	C_8H_8	$0.23*10^{-11}$	1.04	100
Polyisoprene	hPI	C_5H_8	$0.33*10^{-12}$	0.91	75
Dioctylphthalate	DOP	$C_{24}H_{38}O_4$	$4.07*10^{-12}$	0.98	397

The three contrast factors are given by:

$$\left(\frac{b_{hPS}}{v_{hPS}} - \frac{b_{hPI}}{v_{hPI}} \right)^2 N_{av} = 2.08*10^{-4} \, mol/cm^4. \qquad (1)$$

$$\left(\frac{b_{hPS}}{v_{hPS}} - \frac{b_{DOP}}{v_{DOP}} \right)^2 N_{av} = 9.75*10^{-5} \, mol/cm^4.$$

$$\left(\frac{b_{hPI}}{v_{hPI}} - \frac{b_{DOP}}{v_{DOP}} \right)^2 N_{av} = 2.05*10^{-5} \, mol/cm^4.$$

The contrast factors were multiplied by Avogadro's number N_{av} in order to keep the order of magnitude reasonable. Some of these contrast factors are used in the data analysis process.

2. SANS DATA

A SANS data set was acquired using one instrument configuration for which the prominent scattering peak occurs in the middle of the scattering window. Sample temperature was varied between 20 ºC and 70 ºC at 10 ºC intervals.
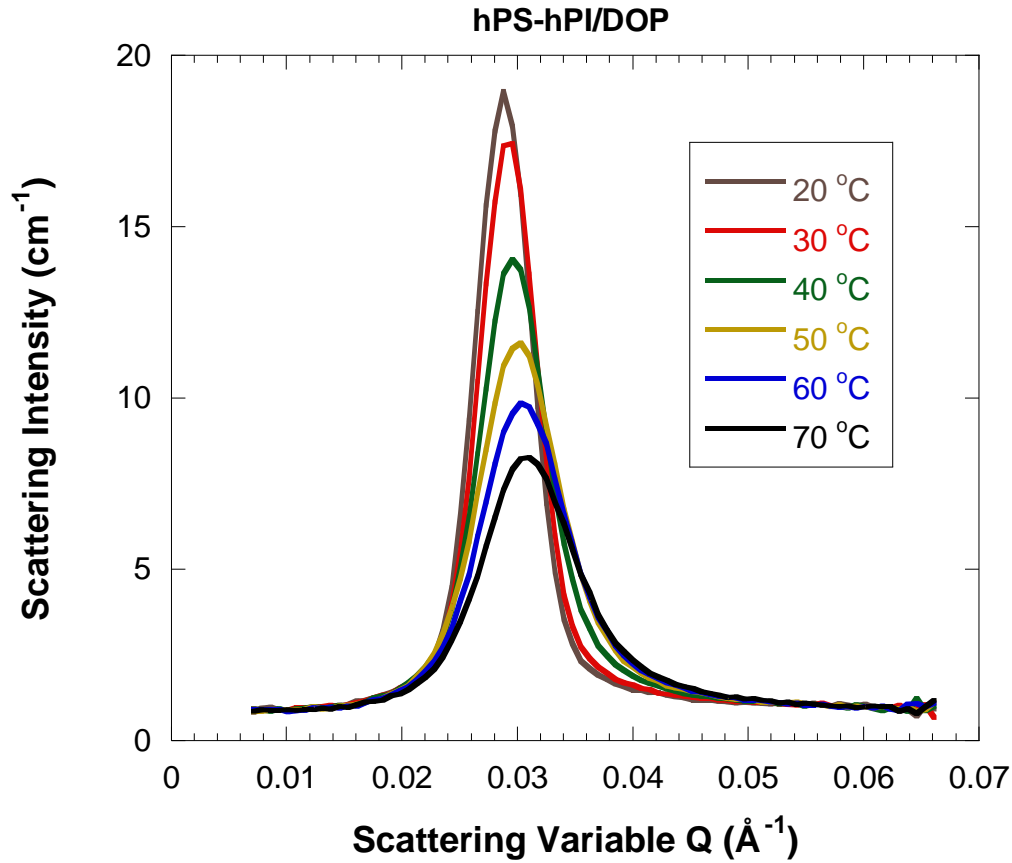

Figure 1: SANS data from the hPS-hPI/DOP diblock copolymer solution at various sample temperatures.

This order-to-disorder transition temperature (ODT) is the equivalent of the spinodal temperature for polymer blends displaying a UCST behavior. When temperature is raised, the copolymer ordered phase melts into a disordered phase.

An empirical model characterized by a peaked behavior is used first to fit the SANS data:

$$I(Q) = \frac{C}{1 + \left(|Q - Q_0| \, \xi \right)^m} + B \, . \qquad (2)$$

The fitting parameter C is a measure of composition fluctuations. C is high in the ordered phase and decreases in the disordered phase. A simple way of estimating the ODT is

through a plot of 1/C *vs* 1/T (T is the absolute temperature). Extrapolation to the condition where the scattering peak intensity C blows up yields an ODT of 29 °C. The hPS-hPI/DOP is ordered below that temperature. The measured sample phase separates into a lamellar morphology.
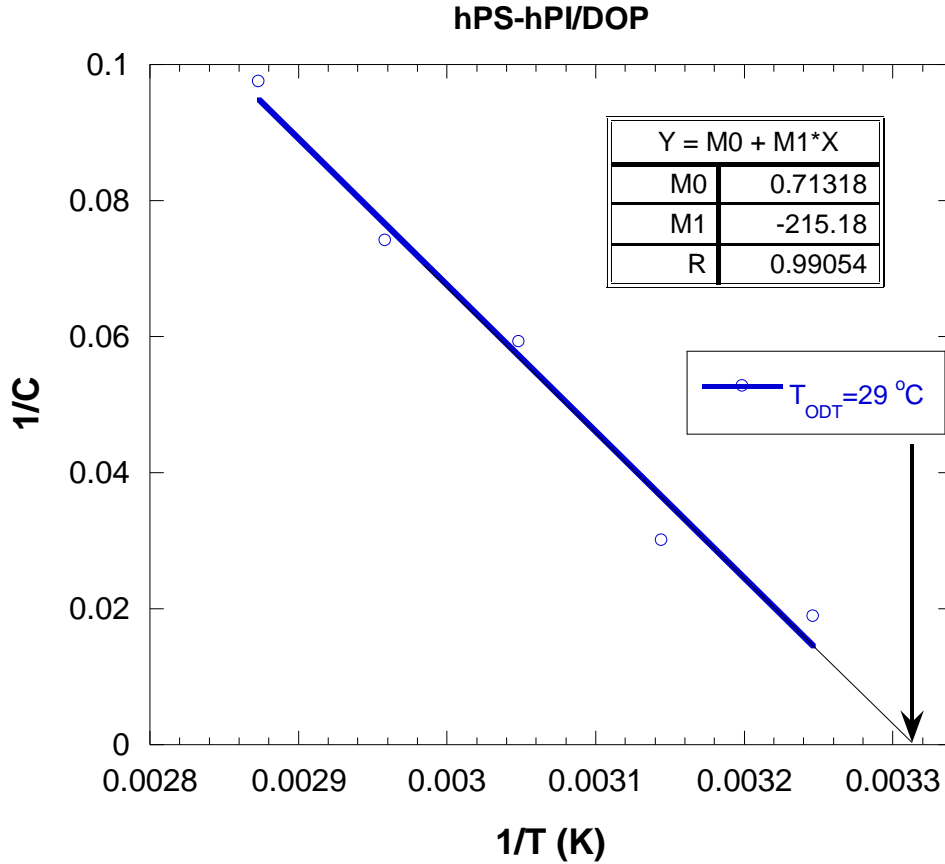
hPS-hPI/DOP

Y = M0 + M1*X	
M0	0.71318
M1	-215.18
R	0.99054

T_{ODT}=29 °C

Figure 2: Determination of the order-to-disorder temperature.

3. THE RPA MODEL FOR A DIBLOCK COPOLYMER SOLUTION

Consider the DOP solvent (component 3) as the background component in the Random Phase Approximation (RPA) model (Akcasu-Tombakoglu, 1990; Hammouda, 1993). The incompressible RPA model applies to the disordered phase only. The relevant equations in matrix form are reproduced here as a review.

$$\underline{\underline{S}}^{-1}(Q) = \underline{\underline{S}}_0^{-1}(Q) + \underline{\underline{v}}(Q) \tag{2}$$

$$\underline{\underline{S}}(Q) = \left(\underline{\underline{1}} + \underline{\underline{S}}_0(Q) \cdot \underline{\underline{v}}(Q)\right)^{-1} \underline{\underline{S}}_0(Q)$$

$$\underline{\underline{S}}_0(Q) = \begin{bmatrix} S_{11}^0(Q) & S_{12}^0(Q) \\ S_{21}^0(Q) & S_{22}^0(Q) \end{bmatrix}$$

$$S_{ii}^0(Q) = n_i \phi_i v_i P_i(Q)$$

$$S_{ij}^0(Q) = \sqrt{n_i \phi_i v_i n_j \phi_j v_j} P_{ij}(Q)$$

$$P_i(Q) = \frac{2}{Q^4 R_{gi}^4} \left[\exp(-Q^2 R_{gi}^2) - 1 + Q^2 R_{gi}^2 \right]$$

$$P_{ij}(Q) = F_i(Q) F_j(Q) = \left(\frac{1 - \exp\left(-Q^2 R_{gi}^2\right)}{Q^2 R_{gi}^2} \right) \left(\frac{1 - \exp\left(-Q^2 R_{gj}^2\right)}{Q^2 R_{gj}^2} \right)$$

$$R_{gi}^2 = \frac{n_i a_i^2}{6}$$

$$v_{11}(Q) = \frac{1}{S_{33}^0(Q)} - 2 \frac{\chi_{13}}{v_0}$$

$$v_{22}(Q) = \frac{1}{S_{33}^0(Q)} - 2 \frac{\chi_{23}}{v_0}$$

$$v_{12}(Q) = \frac{1}{S_{33}^0(Q)} + \frac{\chi_{12}}{v_0} - \frac{\chi_{13}}{v_0} - \frac{\chi_{23}}{v_0}$$

$$S_{11}(Q) = \frac{S_{11}^0\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - S_{12}^0\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}$$

$$S_{22}(Q) = \frac{S_{22}^0\left(1 + v_{12}S_{21}^0 + v_{11}S_{11}^0\right) - S_{21}^0\left(v_{12}S_{22}^0 + v_{11}S_{12}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}$$

$$S_{12}(Q) = \frac{-S_{11}^0\left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right) + S_{12}^0\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)}{\left(1 + v_{11}S_{11}^0 + v_{12}S_{21}^0\right)\left(1 + v_{21}S_{12}^0 + v_{22}S_{22}^0\right) - \left(v_{11}S_{12}^0 + v_{12}S_{22}^0\right)\left(v_{21}S_{11}^0 + v_{22}S_{21}^0\right)}$$

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho_1^2 S_{11}(Q) + \Delta\rho_2^2 S_{22}(Q) + 2\Delta\rho_1 \Delta\rho_2 S_{12}(Q).$$

Note that a Q-independent constant has been added to the scattering intensity to account for the incoherent scattering background. These equations are used to fit the SANS data in the disordered phase.

4. SANS DATA ANALYSIS

Analysis of the SANS data was performed using the RPA model and the following input parameters:

Component 1: hPS, n_{hPS}=106, ϕ_{hPS}=0.23, v_{hPS}=100 cm^3/mol $\qquad$ (3)
Component 2: hPI, n_{hPI}=250, ϕ_{hPI}=0.42, v_{hPI}=75 cm^3/mol
Component 3: DOP, n_{DOP}=1, ϕ_{DOP}=0.35, v_{DOP}=397 cm^3/mol.

The fitting parameters obtained for the 70 °C temperature are included here:

$$a_{hPS} = 8.45 \text{ Å} \qquad (4)$$
$$a_{hPI} = 6.44 \text{ Å}$$
$$a_{DOP} = 29.15 \text{ Å}$$

$$\frac{\chi_{hPS/DOP}}{v_0} = 0.0104 \text{ mol/cm}^3$$

$$\frac{\chi_{hPI/DOP}}{v_0} = 0.040 \text{ mol/cm}^3$$

$$\frac{\chi_{hPS/hPI}}{v_0} = 0.013 \text{ mol/cm}^3$$

$$B = 0.828 \text{ cm}^{-1}.$$

These parameters are reasonable estimates given the fact that so many parameters were floated at the same time. More precise parameters could be obtained if pure hPS/DOP, hPI/DOP and/or hPS/hPI samples were measured first. The 70 °C temperature is above the ODT (of 29 °C) and well within the single-phase region whereby the copolymer microstructure has melted. The observed SANS peak is due to the correlation hole effect.
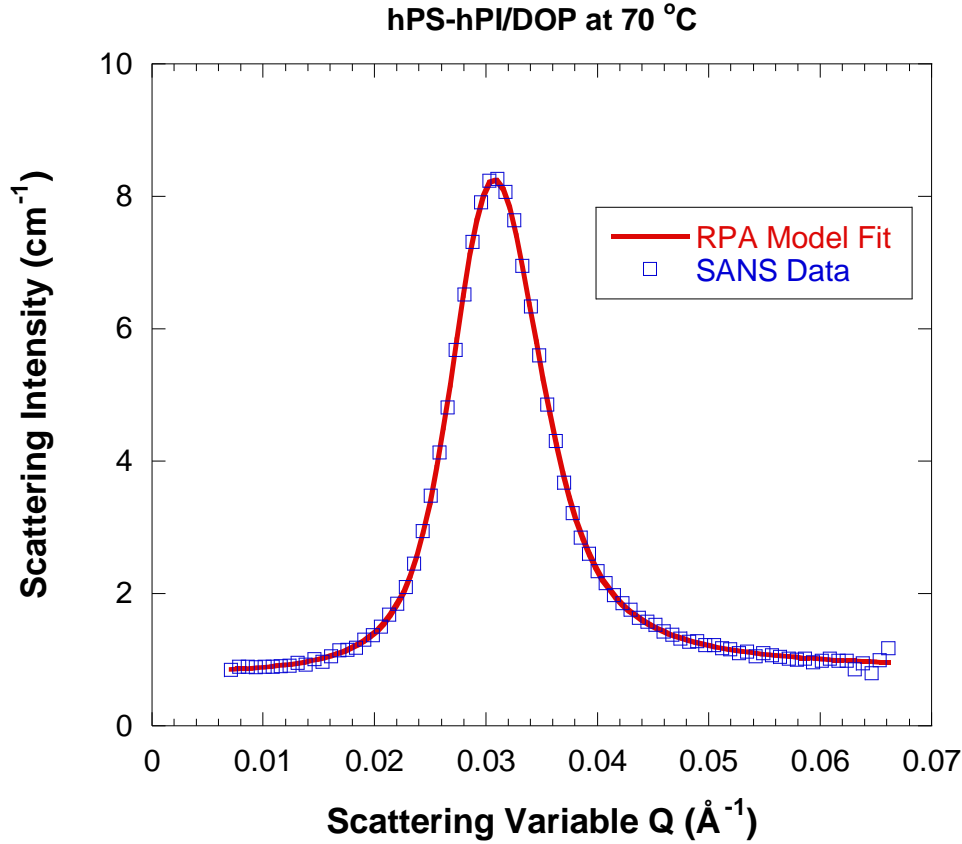
hPS-hPI/DOP at 70 °C

Figure 3: Superposition of the RPA model fit and the SANS data for the 70 °C temperature.

5. THE ORDERED PHASE

The ordered phase is characterized by three main morphologies: spherical, cylindrical or lamellar domains. Other morphologies such as the gyroid and double-diamond phases are also known. The RPA model can predict the ODT line but does not apply in the ordered phase region. It yields predictions from the disordered phase region. Other more sophisticated models such as the self-consistent field theory can predict the various phases in the ordered phase region. The critical condition for a symmetric diblock copolymer is given by $\chi n = 10.5$. Here χ is the Flory-Huggins interaction parameter and n is the degree of polymerization. Recall that this condition is $\chi n = 2$ for symmetric polymer blends. Above that condition, phase separation occurs. Both the spinodal phase separation in polymer blends and the order-to-disorder transition (ODT) in copolymers are second order phase transitions since they involve the second derivative of the Gibbs free energy density $k_B T / S(0) = \partial^2 G / \partial \phi_1^2 = 0$ where ϕ_1 is the order parameter (polymer composition). The ODT is also referred to as a "weak" first order phase transition.

Disordered Block Copolymer
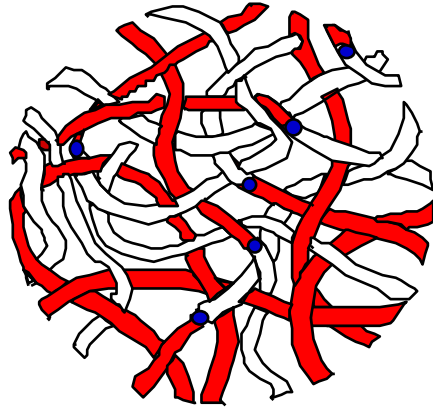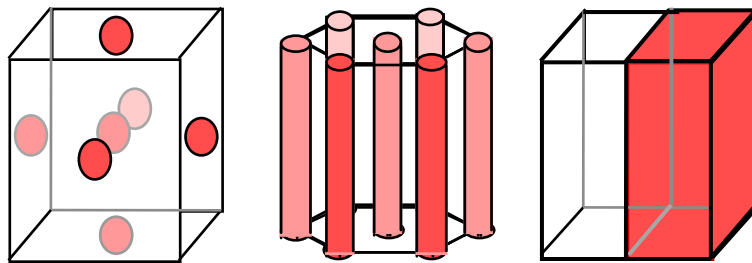

Ordered Block Copolymer

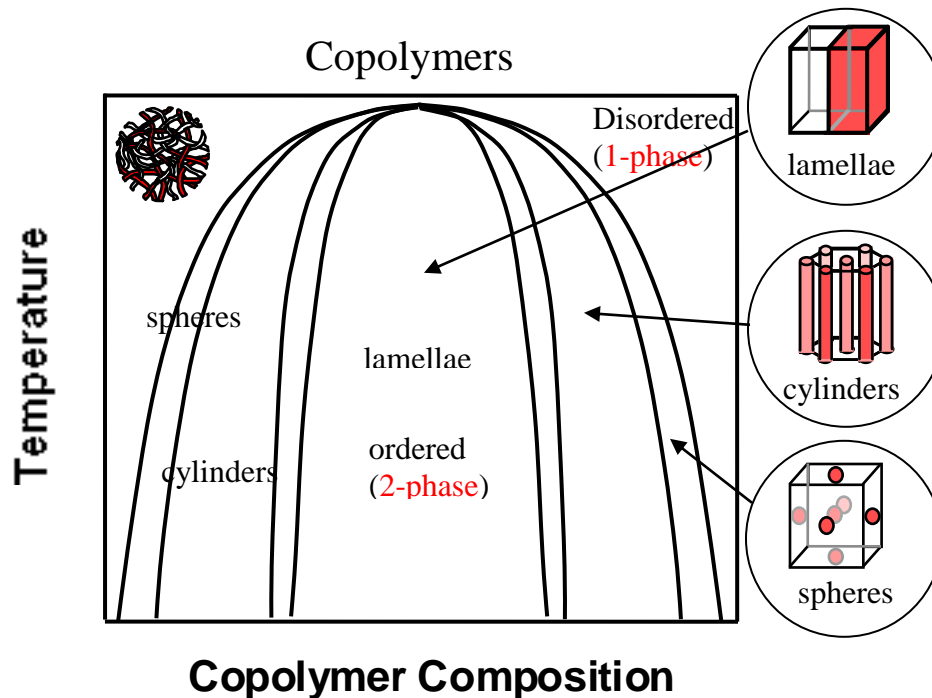Figure 4: Representation of the disordered phase and the ordered phases.

Figure 5: Schematic representation of the copolymer phase boundaries for the main morphologies. The copolymer composition is the volume fraction of one of the blocks.

The position of higher order peaks (relative to the first order peak) varies for the various copolymer morphologies. The first order peaks' sequence occurs as follows:

-- $1, \sqrt{2}, \sqrt{3}, \sqrt{5}$ for the spherical morphology (cubic lattice).

-- $1, \sqrt{3}, \sqrt{4}, \sqrt{7}$ for the cylindrical morphology (hexagonal close-packed lattice).

-- $1, 2, 3, 4$ for the lamellar morphology.

Due to the broad wavelength spread characterizing SANS (and therefore of the standard deviation of the Q resolution), higher order peaks are smeared and hard to resolve.

REFERENCES

L. Leibler, "Theory of Microphase Separation in Block Copolymers", Macromolecules 13, 1602-1617 (1980).

A.Z. Akcasu and M. Tombakoglu, "Dynamics of Copolymer and Homopolymer Mixtures in Bulk and in Solution via the Random Phase Approximation", Macromolecules 23, 607-612 (1990).

B. Hammouda, "SANS from Homogeneous polymer Mixtures: A Unified Overview", Advances in Polymer Science 106, 87 (1993).

QUESTIONS

1. The SANS data from copolymers are characterized by a peak in what phase (ordered or disordered or both)? Why?
2. What is the correlation hole effect?
3. What are the main morphologies formed in the ordered phase region?
4. What is the most likely morphology formed by a symmetric diblock copolymer? Why?
5. What is the critical condition (for phase separation) for χn for symmetric diblock copolymers. Here χ is the Flory-Huggins interaction parameter and n is the degree of polymerization. What is that condition for symmetric polymer blends?
6. What is the order of the spinodal and order-to-disorder phase transitions?

ANSWERS

1. The SANS data from copolymers are characterized by a peak in both the ordered and the disordered phases. The peak in the ordered phase is due to the periodic microphase separated morphology whereas the peak in the disordered phase region is due to the correlation hole effect.
2. The correlation hole effect occurs when the nearest neighbors are excluded from the region right next to a particle. In copolymers, the second block excludes regions containing the first block.
3. The main morphologies formed in the ordered phase region are spherical, cylindrical and lamellar.
4. The most likely morphology formed by a symmetric diblock copolymer is lamellar because there is 50 % of each block.
5. The critical condition (for phase separation) for symmetric diblock copolymers is $\chi n = 10.5$. That condition is $\chi n = 2$ for symmetric polymer blends.
6. The spinodal transition for polymer blends and the order-to-disorder phase transition for copolymers are both second order phase transitions. The ODT is also referred to as a "weak" first order transition.